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Standard molar enthalpy of formation of uniform $CdMoO_4$ nano-octahedra

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Controllable synthesis of uniform and single-crystalline $CdMoO_4$ nano-octahedra has been successfully realized at large-scale by a facile reverse-microemulsion route at room temperature. The structures, compositions and morphologies of the as-prepared products were characterized in detail by X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), respectively. According to the thermochemical cycle, the relationship between the standard molar enthalpy of formation of nano-$CdMoO_4$ and bulk $CdMoO_4$ was proposed for the first time. In combination with micro-calorimetry, the standard molar enthalpies of formation at 298.15 K of as-synthesized $CdMoO_4$ nano-octahedra were obtained.

$CdMoO_4$ nano-octahedra, granularity effect, microcalorimetry, standard molar enthalpy of formation, thermodynamic potential function method

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As important functional materials, metal molybdates have attracted much research attention over the past few decades because of their potential applications in various areas, such as photoluminescence [1,2], optical fibers [3,4], catalysis [5], humidity sensors [6], scintillators [7], and magnetic properties [8]. As a result, a great number of metal molybdates have been successfully prepared [9–16]. However, to the best of our knowledge, few reports focus on cadmium molybdate ($CdMoO_4$), whether on its synthesis or properties.

Thermodynamic properties play important roles in scientific research and industrial applications. Little work has been carried out to investigate the thermodynamic properties of nanomaterials. The earliest studies of "nanothermodynamics" were proposed by Hill [17–19] in 2001. Nevertheless, a theoretical thermodynamic system of nanomaterials has not yet been thoroughly investigated, particularly in specified thermodynamic functions such as entropy, enthalpy or Gibbs free energy. It is important research subject of nanomaterial thermodynamic to explore the relationship between the specified thermodynamic functions of nanomaterials and their sizes or morphologies, establish the basal thermodynamic date standards of nanomaterials which have different scales and morphologies, and thus obtain (experimently) the specified thermodynamic function values of such nanomaterials. In comparison with increasing research on its synthesis, the corresponding properties of $CdMoO_4$ are rarely reported, especially the thermodynamic properties.

On-going work on the thermodynamic data for several nano-metal molybdates, lead the authors to propose this novel method for the standard molar formation enthalpy of $CdMoO_4$ nano-octahedra by micro-calorimetric method. The relationships governing standard molar formation enthalpies between nano- and bulk $CdMoO_4$ were obtained by designing a thermochemical cycle, according to the thermodynamic potential function method, results from which are presented here.

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1 Materials and method

1.1 Reagents and instruments

Sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$, AR), cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$, AR), hydrochloric acid (HCl, 0.26 mol L^{-1}), TritonX-100 (OP, CP), *n*-octanol ($CH_3(CH_2)_7OH$, AR) and cyclohexane (C_6H_{12}, AR) purchased from Xilong Chemical Reagent Factory (Shantou, China) and used without further purification. Deionized water was used to prepare all the aqueous solutions.

Micro-calorimeter (RD496-CK2000, Mianyang CP Thermal Analysis Instrument Co., Ltd, China), inductively coupled plasma (ICP, Perkin Elmer Optima 5300 DV), Philips PW 1710 X-ray powder diffraction meter (XRD, Cu Kα radiation, λ = 1.5406 Å), field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F, Almelo, Netherlands), transmission electron microscopy (TEM, JEOL JEM-200CX, 200 kV, Tokyo, Japan) with energy dispersed X-ray spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010, 200 kV, Tokyo) were used.

All the enthalpies of reaction were measured by the RD496- CK2000 heat conduction micro-calorimeter, which is a totally automatic instrument controlled by computer. To check the performance of micro-calorimeter, the calorimetric constant 63.205 ± 0.031 μV mW^{-1} at 298.15 K was determined by the Joule effect before the experiments. The calorimeter was calibrated by measuring the dissolution enthalpy of KCl(s) in deionised water, and the experimental value 17.469 ± 0.036 kJ mol^{-1} was in agreement with the value of 17.524 ± 0.028 kJ mol^{-1} reported elsewhere [20].

1.2 Microemulsion synthesis

The molar ratio of water to OP (or the water content (ω)) played a crucial role in the formation process of $CdMoO_4$ nano-octahedra. Experiments were performed using the following synthetic procedures, two microemulsion solutions were prepared by adding the same volume 0.1 mol L^{-1} $Cd(NO_3)_2$ and 0.1 mol L^{-1} Na_2MoO_4 aqueous solutions into a cyclohexane/OP/*n*-octanol system (molar ratio of *n*-octanol to OP = 3.9), respectively. For ω = 5, the volume of the aqueous solutions was 0.30 mL; ω = 10, the volume of the aqueous solutions was 0.60 mL; ω = 20, the volume of the aqueous solutions was 1.20 mL, and bulk $CdMoO_4$ with $\omega \to \infty$ were prepared through mixing the $Cd(NO_3)_2$ and Na_2MoO_4 aqueous solutions together directly. After 30 min stirring, the aforementioned microemulsion solutions with equivalent volume were mixed slowly and stirred for 10 min. The resulting mixture was aged without stirring for 48 h at room temperature. The precipitates were separated by centrifugation, and washed with acetone, deionized water and absolute ethanol several times to remove any impurities. The final products were dried in a vacuum drying oven at room temperature, and the synthetic products were characterized by XRD, SEM, HR-TEM, and TEM with EDS, respectively.

1.3 Method of calorimetric experiments

The standard molar enthalpies for the reaction between $CdMoO_4$ and HCl were measured by micro-calorimeter. A certain amount of $CdMoO_4$ samples with different ω and HCl were put in two separate glass containers in a 15 mL stainless steel sample cell. The HCl (2.0 mL) was put in a small glass tube above the $CdMoO_4$, which was in a larger glass tube. After equilibration, the small glass tube was broken by a steel rod, and the HCl rapidly mixed with those solid samples in the larger glass tube. Then the thermodynamic information for the reaction process was recorded automatically by the micro-calorimeter. The calorimetric experiment for each ω system was performed five times at normal temperature and pressure. No solid residue remained after each calorimetric experiment, and upon completion, the concentration of cadmium ions in each reaction system was measured by ICP.

1.4 Thermochemical cycles

The relevant reactions and thermochemical equations which have been used to derive the standard molar formation enthalpy of $CdMoO_4$ nano-octahedra are as follows:

$$CdMoO_4(bulk) + 2HCl(aq) = CdCl_2(aq) + H_2MoO_4(aq)$$

$$\Delta_r H_m^{\theta}(bulk) = 2\Delta_f H_m^{\theta}(CdCl_2) + \Delta_f H_m^{\theta}(H_2MoO_4) - 2\Delta_f H_m^{\theta}(HCl) - \Delta_f H_m^{\theta}(CdMoO_4, bulk), \quad (1)$$

$$CdMoO_4(nano) + 2HCl(aq) = CdCl_2(aq) + H_2MoO_4(aq)$$

$$\Delta_r H_m^{\theta}(nano) = \Delta_f H_m^{\theta}(CdCl_2) + \Delta_f H_m^{\theta}(H_2MoO_4) - 2\Delta_f H_m^{\theta}(HCl) - \Delta_f H_m^{\theta}(CdMoO_4, nano). \quad (2)$$

Applying Hess's law, the following expression is found:

$$\Delta_f H_m^{\theta}(CdMoO_4,nano) = \Delta_f H_m^{\theta}(CdMoO_4,bulk) + \Delta_r H_m^{\theta}(bulk) - \Delta_r H_m^{\theta}(nano), \quad (3)$$

where $\Delta_r H_m^{\theta}$(nano) represent the standard molar enthalpy of the reaction between $CdMoO_4$ nano-octahedra and HCl, $\Delta_r H_m^{\theta}$(bulk) represents the standard molar enthalpy of reaction between bulk $CdMoO_4$ and HCl, $\Delta_f H_m^{\theta}$ ($CdMoO_4$, nano) represents the standard molar formation enthalpy of nano-$CdMoO_4$, and $\Delta_f H_m^{\theta}$($CdMoO_4$, bulk) represents the standard molar formation enthalpy of bulk $CdMoO_4$.

According to the thermodynamic potential function method, the thermochemical cycle was designed (Figure 1).

2 Results and discussion

2.1 Morphology and structure

Figure 2(a) is the typical powder XRD pattern of the as-obtained $CdMoO_4$ nano-octahedra, on which all the diffraction peaks could be indexed to tetragonal-phase $CdMoO_4$ (JCPDS No. 07-0209). The XRD patterns of other samples

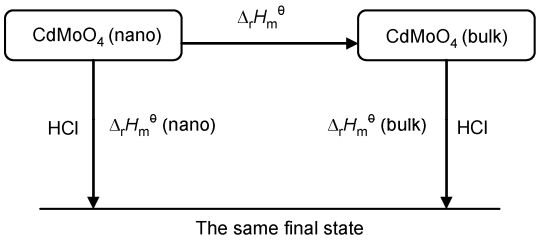

Figure 1 Schematic illustration of thermochemical cycle between the nano- and bulk reaction system.

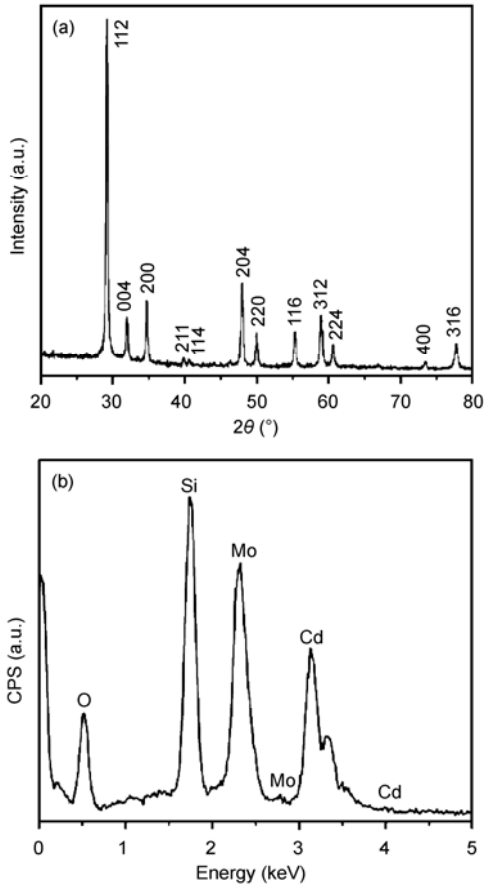

Figure 2 Powder XRD pattern (a) and EDS spectrum (b) of the as-obtained products.

obtained under different ω conditions were similar to that of Figure 2(a), and no characteristic peaks arising from other impurities were detected therein, which implied a high-purity final product. The composition of the $CdMoO_4$ nanostructure was further characterised using EDS, and the result shown in Figure 2(b). The EDS spectrum exhibited strong peaks from Cd, Mo, and O. The Si signals arose from the Si substrate. Quantitative analysis showed that the atomic ratio of Cd to Mo to O was approximately 1∶1∶4, being consistent with the stoichiometric composition of $CdMoO_4$.

The size of the $CdMoO_4$ nano-octahedra can be simply tuned by varying the value of ω. Figure 3 are the SEM and TEM images of the as-prepared products obtained at different values of ω, respectively. For ω = 5, smooth nano-octahedra with edge-lengths of 200 nm were observed (Figure 3(a)). The edge-length of monodisperse $CdMoO_4$ nano-octahedra was 30 nm when ω was increased to 10 (Figure 3(b)). When ω was further increased to 20, nano-octahedra with a side length of 25 nm were obtained (Figure 3(c)). However, as $\omega \to \infty$, heterogeneous $CdMoO_4$ near-spherical aggregates were formed with rough surfaces and diameter of 1 to 6 μm (Figure 3(d)).

2.2 Standard molar enthalpies of formation

Table 1 gives the results of the calorimetric measurements. The uncertainty is twice the standard deviation of the mean value, namely

$$\delta = 2\sqrt{\sum \frac{\left(x_i - \overline{x}^2\right)}{n(n-1)}}, \tag{4}$$

in which x_i represents the experimental value of each series of repeated measurement, n is experimental number (n = 5), and $\overline{x}$ denotes the mean value. The auxiliary datum taken from the literature is: the standard molar enthalpy of formation of $CdMoO_4$(bulk) –(1034.3 ± 5.7) kJ mol^{-1} [20]. So the standard molar enthalpy of formation of $CdMoO_4$ (nano) is calculated to be:

ω = 5,

$\Delta_f H_m^\theta(CdMoO_4, nano)$
$= \Delta_f H_m^\theta(CdMoO_4, bulk) + \Delta_r H_m^\theta(bulk) - \Delta_r H_m^\theta(nano)$
$= -(1034.3 \pm 5.7) + (-15.54 \pm 0.10) - (-63.90 \pm 0.95)$
$= -(985.94 \pm 5.8)$ kJ mol^{-1}

ω = 10,

$\Delta_f H_m^\theta(CdMoO_4, nano)$
$= \Delta_f H_m^\theta(CdMoO_4, bulk) + \Delta_r H_m^\theta(bulk) - \Delta_r H_m^\theta(nano)$
$= -(1034.3 \pm 5.7) + (-15.54 \pm 0.10) - (-80.83 \pm 0.18)$
$= -(969.01 \pm 5.7)$ kJ mol^{-1}

ω = 20,

$\Delta_f H_m^\theta(CdMoO_4, nano)$
$= \Delta_f H_m^\theta(CdMoO_4, bulk) + \Delta_r H_m^\theta(bulk) - \Delta_r H_m^\theta(nano)$
$= -(1034.3 \pm 5.7) + (-15.54 \pm 0.10) - (-89.40 \pm 0.50)$
$= -(960.44 \pm 5.7)$ kJ mol^{-1}

These results demonstrate that the standard molar formation enthalpy of $CdMoO_4$ nanostructure was higher than that of the bulk material. A feasible explanation may have been that with the decrease in size of $CdMoO_4$ nano-octahedra, the number of atoms on the surface of the crystals increased sharply, thus the $CdMoO_4$(nano) was in a relatively higher energy state because of its high surface energy. Furthermore, the standard molar enthalpy of $CdMoO_4$ nano-octahedra synthesised in this work increased with the ω value: this corroborated the idea that the size of $CdMoO_4$

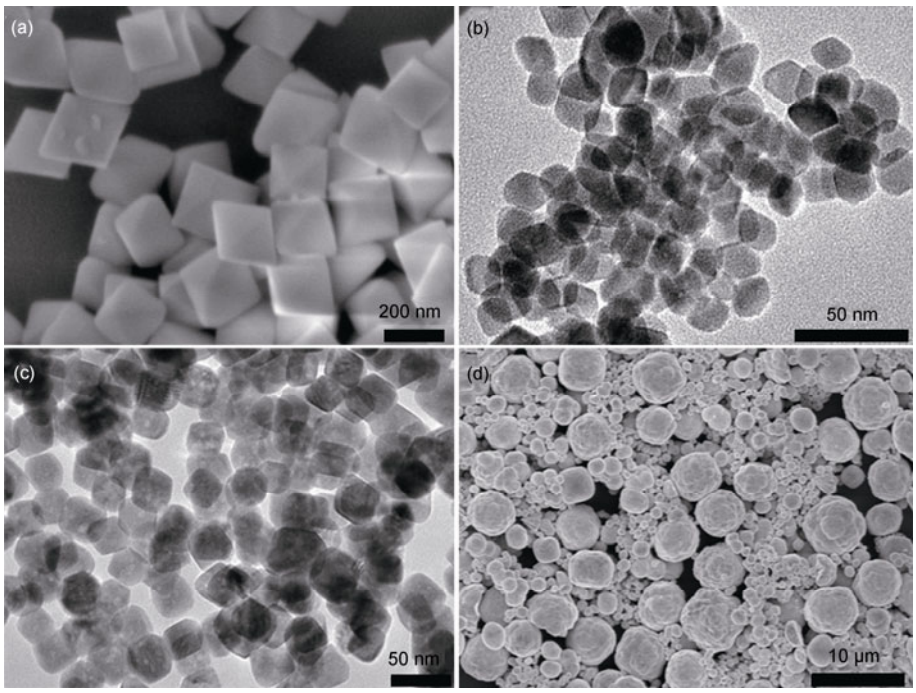

Figure 3 FE-SEM and TEM images of the products prepared at different water contents (ω). (a) ω = 5, (b) ω = 10, (c) ω = 20, (d) $\omega \rightarrow \infty$.

Table 1 The molar enthalpy of reaction of the $CdMoO_4$ nano-octahedra and bulk $CdMoO_4$ systems

Reaction system	$\Delta_r H_m^{\theta}$ (kJ mol^{-1})					
	1	2	3	4	5	Average value
ω = 5	−62.95	−65.41	−63.73	−64.12	−63.28	−63.90 ± 0.95
ω = 10	−81.07	−80.69	−80.62	−80.93	−80.84	−80.83 ± 0.18
ω = 20	−88.65	−89.63	−89.99	−89.51	−89.19	−89.40 ± 0.50
Bulk	−15.39	−15.66	−15.56	−15.50	−15.57	−15.54 ± 0.10

nano-octahedra decreased with increasing ω which was consistent with the conclusion drawn by the characterisation of the synthetic samples using SEM and TEM in a previous report [22]. Further studies revealed that the difference between the standard molar enthalpies of formation of $CdMoO_4$ between ω = 10 and 20 was only 8.75 kJ mol^{-1}, because of the approximate size. Accordingly, we can speculate that there may be some quantitative relationship between the standard molar enthalpies of nanomaterials and their size, however, this would need further research to verify the hypothesis.

3 Conclusions

In conclusion, well-shaped, homogeneous single- crystalline $CdMoO_4$ nano-octahedra have been successfully prepared by a facile nonionic Triton X-100-based reverse microemulsion route at room temperature. Through an appropriate thermochemical cycle, standard molar enthalpies of formation of the $CdMoO_4$ nano-octahedra have been obtained by micro-calorimetry. The recommended values of the as-prepared samples were: −(985.94 ± 5.8) kJ mol^{-1} at ω = 5, −(969.01 ± 5.7) kJ mol^{-1} at ω = 10, and −(960.44 ± 5.7) kJ mol^{-1} at ω = 20. Under equi-morphological conditions, it was found that the size played an important role in determining the standard molar enthalpies of formation of the as-fabricated octahedral $CdMoO_4$ nano crystals. The present work was not only helpful in systematically exploring the standard molar enthalpies of formation of nanomaterials, but also provided a novel and universal method of obtaining the standard molar enthalpies of formation of other nanomaterials.

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